metric analyses of the products provide evidence concerning the nature of the primary processes. The results confirm the conclusions of Leighton, *et al.*,[1] and Blacet and Calvert[2] and provide new evidence for the occurrence of several modes of primary photodecomposition: (1) Primary processes producing formyl radicals and *n*-propyl radicals, from *n*-butyraldehyde, and isopropyl radicals, from isobutyraldehyde, are important at wave lengths of absorbed light from 2537 to 3130 Å. (2) Intramolecular primary processes producing carbon monoxide and propane are unimportant in the photolyses of both butyraldehydes at wave length 3130 Å. but increase in importance at the shorter wave lengths. (3) Intramolecular formation of ethylene and acetaldehyde is important in *n*-butyraldehyde photolysis at wave lengths from 2537 to 3130 Å. (4) A primary process in which methyl radicals are formed is of importance in isobutyraldehyde photolysis at wave length 2537 Å.

A correlation between total primary quantum yields of decomposition of the butyraldehydes, fluorescence data and character of the absorption spectra is indicated.

LOS ANGELES 24, CALIFORNIA RECEIVED AUGUST 14, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Mechanisms of Elimination Reactions. III. The Kinetics of the Alkaline Dehydrochlorination of the Benzene Hexachloride Isomers. II.[1,2,3]

BY STANLEY J. CRISTOL, NORMAN L. HAUSE AND JOHN S. MEEK

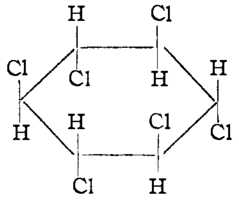
Previous work[1b,4-7] has indicated a stereochemical preference in the E2 (second-order) elimination[8] of the elements of hydrogen halides from alkyl halides, *trans* elements being removed more readily than corresponding *cis* elements. Several suggestions have been made as to the cause of this preference, one[7] involving *cis* repulsions and one[1b] being based on a one-stage mechanism for the *trans* process and a multiple-stage mechanism for the *cis* process.

As it seemed likely that information regarding the importance of these effects on elimination could be gained by a knowledge of the quantities of activation (energy and entropy), we have undertaken a study of alkaline dehydrohalogenation of a number of *cis* and *trans* systems at various temperatures, and this paper considers the first series of such compounds.

The compounds used were four of the five known isomers of benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane), hereinafter called BHC.

The structures of all of the known isomers have now apparently been established,[9] although dipole moment results are not at all clear.[14] The structures as given by Hassel and co-workers[10] are: alpha, $\frac{124}{356}$; beta, $\frac{135}{246}$; gamma, $\frac{1245}{36}$; delta, $\frac{1235}{46}$; and epsilon, $\frac{123}{456}$, where the numbers above the line indicate the positions of chlorine atoms which lie above a hypothetical planar cyclohexane ring and those below the line lie below the hypothetical planar cyclohexane ring.

For the purpose of this paper, we need be concerned only with the fact that β-BHC has the structure



where no members of a pair of hydrogen and chlorine atoms on adjacent carbon atoms are *trans* to each other, and that in each other isomer, at least one pair comprises *trans* hydrogen and chlorine atoms.

The reaction studied in the present work is the elimination of three moles of hydrogen chloride from each isomer according to equation (1).

$$C_6H_6Cl_6 + 3OH^- \longrightarrow C_6H_3Cl_3 + 3Cl^- + 3H_2O \quad (1)$$

van der Linden[15] has shown that the α-, β- and γ-isomers give slightly different ratios of 1,2,4-, 1,2,3- and 1,3,5-trichlorobenzenes, but that in each case the 1,2,4-isomer is predominant. The present work is restricted to a study of the kinetics of the reaction; except for the test that three moles of chloride ion were formed per mole of BHC, no investigation of the products was made.

Measurement of Reaction Rates and Calculation of Rate Constants.—The reactions were carried out in 76.1% (by wt.) ethanol using

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(1) Previous papers in series: (a) Cristol, THIS JOURNAL, **67**, 1494 (1945); (b) Cristol, *ibid.*, **69**, 338 (1947).

(2) This work was supported by the Office of Naval Research.

(3) This work was reported in part before the Division of Organic Chemistry at the Atlantic City Meeting of the American Chemical Society, September, 1949.

(4) Wislicenus, *Ann.*, **248**, 281 (1888).

(5) Michael, *J. prakt. Chem.*, **52**, 289 (1895).

(6) Chavanne, *Bull. soc. chim. Belg.*, **26**, 287 (1912).

(7) Hückel, Tappe and Legutke, *Ann.*, **543**, 191 (1940).

(8) Hughes and Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

(9) The structure of the α-isomer has been established by electron diffraction work[10] and by resolution into an optically active form.[11] The structure of the β-isomer has been established by X-ray diffraction,[12] that of the γ-isomer by X-ray analysis[13] and by electron diffraction,[10] and those of the δ and ε isomers by electron diffraction.[10]

(10) Bastiansen, Ellefsen and Hassel, *Research*, **2**, 248 (1949).

(11) Cristol, THIS JOURNAL, **71**, 1894 (1949).

(12) Hendricks and Bilicke, *ibid.*, **48**, 3007 (1926); Dickinson and Bilicke, *ibid.*, **50**, 764 (1928).

(13) van Vloten, Kruissink, Strijk and Bijvoet, *Nature*, **162**, 771 (1948); Bijvoet, *Rec. trav. chim.*, **67**, 777 (1948).

(14) (a) Melander, *Svensk. Kem. Tids.*, **58**, 231 (1946); (b) Hetland, *Acta Chem. Scand.*, **2**, 678 (1948); (c) Jatkar and Kulkarni, *Science and Culture*, **14**, 482 (1949); (d) Rolla, Fontana and Marinangeli, *Gazz. Chim. Ital.*, **79**, 491 (1949).

(15) van der Linden, *Ber.*, **45**, 231 (1912).

sodium hydroxide as base, and the extent of the reaction was estimated by chloride ion titration, substantially as described previously.[1b] The reactions were conducted in various thermostatted baths which were controlled to ±0.02°.

The course of the dehydrochlorination is

$$C_6H_6Cl_6 + OH^- \xrightarrow{k_1} C_6H_5Cl_5 + Cl^- + H_2O \quad (2a)$$

$$C_6H_5Cl_5 + OH^- \xrightarrow{k_2} C_6H_4Cl_4 + Cl^- + H_2O \quad (2b)$$

$$C_6H_4Cl_4 + OH^- \xrightarrow{k_3} C_6H_3Cl_3 + Cl^- + H_2O \quad (2c)$$

where it is possible for any of the above steps to be slow and rate-determining.

Analysis of the rate equation for the second-order reaction represented by (2a) as the rate-determining step—first order with respect to both hydroxide ion and BHC concentrations—and followed by rapid steps (2b) and (2c) gives the following equation connecting initial BHC concentration a, initial hydroxide concentration b, fraction φ of BHC reacted, and time t.

$$\mathrm{d}\log\frac{1 - 3a\varphi/b}{1 - \varphi}/\mathrm{d}t = \frac{b - 3a}{2.303}k_1 \quad (3)$$

If these kinetics hold, a plot of the values of log $(1 - 3a\varphi/b)/(1 - \varphi)$ corresponding to the various samples of a run against corresponding values of time t should give a straight line. The slope of the line multiplied by the value of $2.303/(b - a)$ for the run gives the rate constant k_1. Values for k_1 are given in Table I. Deviations from the straight line relationship are measures of the lack of correspondence to the assumption that k_2 and k_3 are much greater than k_1.

TABLE I

DATA AND REACTION-RATE CONSTANTS FOR DEHYDROCHLORINATION OF BENZENE HEXACHLORIDE ISOMERS WITH SODIUM HYDROXIDE IN 76.1% ETHANOL

Isomer	Temp., °C.	[Halide] a, M	[NaOH] b, M	10^5k l./sec./mole	Av.	Average deviation, %
α	1.13	0.001024	0.004932	1810	1880	3.7
		.001018	.004932	1950		
	10.07	.001113	.004858	6010	5920	1.5
		.001128	.004858	5830		
	20.11[a]	.000760	.00471	16700	17000	1.5
		.000980	.00471	17200		
β	29.69	.001046	.05621	1.97	2.00	1.7
		.0009592	.05621	2.04		
	40.12	.001032	.05621	10.8	10.9	0.9
		.001183	.05621	11.0		
	48.81	.001119	.05621	42.1	42.5	0.9
		.001138	.05621	42.9		
γ	10.08	.0009874	.009716	1440	1440	0.3
		.0009978	.009716	1430		
	20.11[a]	.000972	.00471	4570	4460	2.5
		.000939	.00471	4350		
	29.72	.001000	.005609	15100	15100	2.0
		.001036	.005621	15500		
		.001007	.005621	14600		
ε	10.08	.0009290	.009716	1380	1420	2.8
		.0009881	.009716	1460		
	20.30	.001033	.005661	5640	5650	0.2
		.001017	.005661	5660		
	29.70	.001002	.005621	16800	17000	1.5
		.0009950	.005621	17300		

[a] Data obtained from previous work.[1b]

If k_2 is smaller than k_1 and k_3, the plot will show a large initial slope (representing the loss of the first molecule of hydrogen chloride) followed by a linear section representing steps (2b) and (2c). Under these conditions, good yields of the intermediate $C_6H_5Cl_5$ compound should be isolable. We have noted such a kinetic relationship previously[1b] in the treatment of δ-BHC with ethanolic alkali and have suggested the possibility of isolation of this material. We have now verified the assumption made by the isolation of a pentachlorocyclohexene, m. p. 68–68.5°, from the treatment of δ-BHC with one mole of sodium hydroxide.[16]

If k_3 is very large, and k_2 is larger than, but of the same order of magnitude as k_1, the initial slope will be low and will increase until the "steady-state" concentration of the intermediate $C_6H_5Cl_5$ is built up. In this case as well, an isolable intermediate will be formed, although in lesser amount than in the first one considered above.

Plots of one run with the β-isomer and of one with the ε-isomer are given in Fig. 1. Excellent correspondence to the straight line relationship was found with these isomers, as well as with the α-isomer. The γ-isomer gave results (see Fig. 2) which seemed to differ from a straight line only insignificantly (with a slight upward bow) when our results were calculated on the assumption that

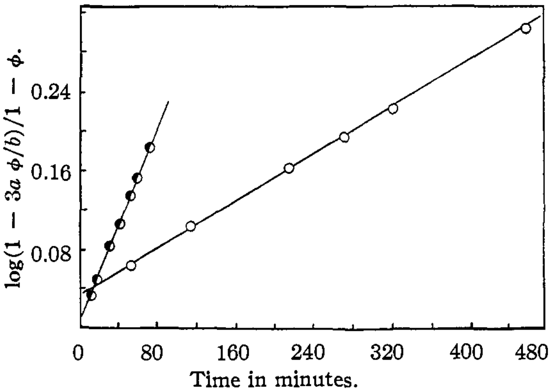

Fig. 1.—Treatment of data for rate constants for ε-isomer at 10.08° (upper line) and for β-isomer at 48.81° (lower line).

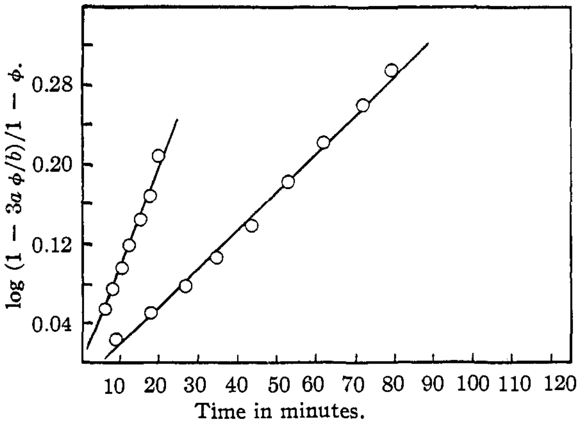

Fig. 2.—Treatment of data for rate constants for γ-isomer at 29.72° (upper line) and 23.32° (lower line).

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[16] This material was recently isolated[17] from the treatment of δ-BHC with sodium hydroxide in aqueous acetone.

[17] Nakajima, Okubo and Katumura, *Botyu-Kagaku*, [14] 10 (Dec., 1949).

k_2 and k_3 are greater than k_1 by a sufficient margin such that our value for k_1 is satisfactory. This assumption seemed reasonable in view of the work of van der Linden,[15] who reported that he was unable to isolate intermediates in the dehydrochlorination of α-, β- and γ-BHC with ethanolic alkali.

Recently Nakajima, Okuba and Katamura[17] studied the dehydrochlorination of γ- and δ-BHC in aqueous dioxane, following the reaction polarographically. This tool offers a real advantage over titration for chloride ion, in that any reducible intermediate may be detected and the rate of its concentration increase and decline may be measured. Its drawbacks will be discussed below (see footnote 18). Nakajima and his co-workers found that the γ-isomer (as well as the δ) formed a stable intermediate of analysis $C_6H_5Cl_5$, in measurable amounts, when treated in 40% aqueous dioxane with sodium borate–sodium hydroxide buffers in the *p*H range 12.1 to 13.7, and were able to isolate the intermediate upon treatment of γ-BHC with sodium hydroxide in aqueous acetone. Their data suggest that k_2 is only slightly larger than k_1 for γ-BHC, and that our values for k_1 are somewhat inaccurate for this reason.[18]

The experimental energies of activation, $E_{\text{act.}}$, were calculated from the data of Table I. Plots of log k against the reciprocal of the absolute temperature gave straight lines whose slopes multiplied by $2.303R$ gave the values of $E_{\text{act.}}$ recorded in Table II. These values, combined with values of k corresponding to values of temperature of 30° (obtained from the plots of log k *vs.* $1/T$) were used in the equation[20]

$$k = e\frac{k'T}{h}\,e^{-E_{\text{act.}}/RT}\,e^{\Delta S^{\ddagger}/R} \qquad (4)$$

where k' is Boltzmann's constant and h is Planck's constant, to calculate values of entropies of activation $\Delta S^{\ddagger}$. These values are given in Table II.

TABLE II

REACTION-RATE CONSTANTS, ENERGIES AND ENTROPIES OF ACTIVATION FOR THE DEHYDROCHLORINATION OF THE BENZENE HEXACHLORIDES AT 30°

Isomer	$k_{30.00°}$, l./sec./mole	$E_{\text{act.}}$, kcal./mole	$\Delta S^{\ddagger}$, cal./deg.
Alpha	0.500	18.5	−1.0
Beta	2.11×10^{-5}	31.0	20.2
Gamma	0.151	20.6	3.6
Epsilon	0.182	21.4	6.5

We estimate the experimental uncertainties in $E_{\text{act.}}$ at less than 1 kcal./mole, with corresponding uncertainties of $\Delta S^{\ddagger}$ at less than 3 e.u./mole.

Discussion of Results.—As we have shown that the first step (2a) is rate-determining for the α-, β- and ε-isomers, and approximately so for the γ-isomer, and as we are concerned with differences between *cis* and *trans* isomers, it is important for the purpose of this paper to know only that at least one pair of vicinal hydrogen and chlorine atoms are *trans* for the α-, γ- and ε-isomers, as only the rate of removal of the first pair is measurable kinetically under our conditions. We have limited our study to these three isomers and to the β-isomer, where no vicinal pair is *trans*.

It is to be noted that β-BHC reacts with hydroxide ion at a rate 7000 to 24,000 times slower than the other isomers, that is, that *trans* elimination is favored in rate at 30° by approximately 10^4. This superiority is due entirely to a favorable activation energy term and is reduced somewhat by the entropy term. The energy of activation for *cis* elimination, that is, for the β-isomer, is 9.6 to 12.5 kcal./mole higher than that for *trans* elimination, and we wish to inquire as to the reasons for the tremendously higher activation energy.[21]

One factor which has been suggested as being of importance in *cis* and *trans* eliminations is that of repulsive forces. Hückel and his co-workers[7] have pointed out that in isomers in which the proton which is removed by an anionoid reagent is *cis* to the halogen atom, the negative end of the carbon–halogen dipole repels the anionoid reagent and thus reduces the probability of reaction. In addition to this electrostatic repulsion the steric repulsions between groups must be considered, and the total of these repulsions, being greater for *cis* than for *trans* halogens, makes *trans* elimination favored over *cis*.

It is not clear as to how these effects will appear quantitatively in the activation energy or activation entropy terms of the Eyring rate expression.[20] A recent discussion of the problem of steric repulsive forces in transition states indicates that the effect of such forces on activation energies are rather minor unless serious compressions are involved.[22] In general, serious compressions are not involved in second-order elimination reactions, which involve attack by a hydroxide ion upon a proton considerably removed from the substituent on the vicinal carbon atom.

The effect of electrostatic repulsions on the activation energy has been estimated from the Coulomb law and shown to be of minor significance. These estimations were made as follows: Diagrams (see Figs. 3 and 4) which show the approach of the hydroxyl group to the alkyl halide to within the transition-state distance of carbon atom C_1 were set up for both *cis* and *trans* elimination cases. These were constructed using normal covalent bond lengths for all bonds except the hydroxyl oxygen-hydrogen-carbon (C_1) bond distances which were increased 10% over normal covalent bond dis-

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(18) Nakajima's use of the polarographic technique for following the rate of the reaction offers a real advantage in the detection of intermediates. However, the system studied is seriously complicated by the need for use of buffers and inert salts. As the elimination process is of the general basic catalysis type,[19] that is, the base initiating the reaction may be any base and not only hydroxyl ion, the type and amount of buffer will have a large influence upon the rate of elimination. This apparently has not been considered by Nakajima and his co-workers. Their data obtained at various *p*H values in aqueous dioxane do not give consistent values for second-order reaction-rate constants independent of *p*H, nor do their rate constants (at *p*H 12.7) at various temperatures seem to fit an activation energy plot. We would attribute these difficulties to the complications produced by the buffer, inert salts and poor temperature control.

(19) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 215.

(20) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

(21) This is equivalent, at equal $\Delta S^{\ddagger}$ and at 30°, to rate differentials of 8.3×10^6 to 1.0×10^9.

(22) Dostrovsky, Hughes and Ingold, *J. Chem. Soc.*, 173 (1946).

tances,[23] and distances between the chlorine atom of the alkyl halide and the oxygen atom of the entering hydroxide ion were determined from them.[24]

The *trans* case (see Fig. 3) was assumed to have the centers of all of the atoms involved lying in the same plane. The oxygen–hydrogen–carbon (O–H–C_1) distance was taken as 2.27 Å., the carbon–carbon bond distance as 1.54 Å., the carbon–chlorine (C_2–Cl) as 1.77 Å., and all angles as tetrahedral. From these values the oxygen–chlorine distance was calculated by the cosine law as 4.78 Å.

In the *cis* case all of the atoms concerned do not lie in the same plane, the angle which the carbon (C_2)–chlorine bond makes with the plane of the other atoms being 54°44′. Use of appropriate trigonometric functions gives an oxygen–chlorine distance of 3.22 Å. for the *cis* case.[25]

The coulombic energy E_c for carrying a negative ion up to a carbon–chlorine dipole may be expressed approximately by the equation

$$E_c = E^- - E^+ \qquad (5)$$

where E^- is the energy required to carry a negative charge up to the negative end of a dipole and E^+ is the energy gained by a negative charge approaching the positive end of a dipole. E^+ is the same for both *cis* and *trans* isomers, since the oxygen–carbon distance is identical in both models, but E^- is different, as the oxygen–chlorine distances are different. Therefore we may write

$$\Delta E_c = E_c(cis) - E_c(trans) = E^-_{cis} - E^-_{trans} \qquad (6)$$

where ΔE_c represents the additional coulombic work required in the *cis* case over the *trans* case to bring a univalent ion from infinity to the model distance from the negative end of a carbon–chlorine dipole.

An expression for the coulombic energy between reactants can be obtained,[27] and when this expression is modified for coulombic interactions between the negative end of a dipole and a charged ion, it may be written in the form

$$E_c = -\frac{NZ_1(\mu/\epsilon d)\epsilon^2}{Dr} \qquad (7)$$

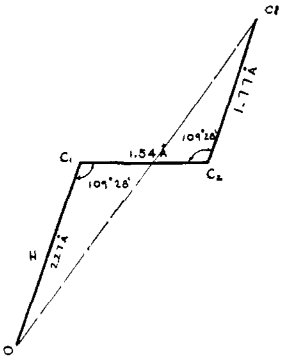

Fig. 3.—Diagram showing approximate transition-state distances involved in energy calculations for the *trans* configuration.

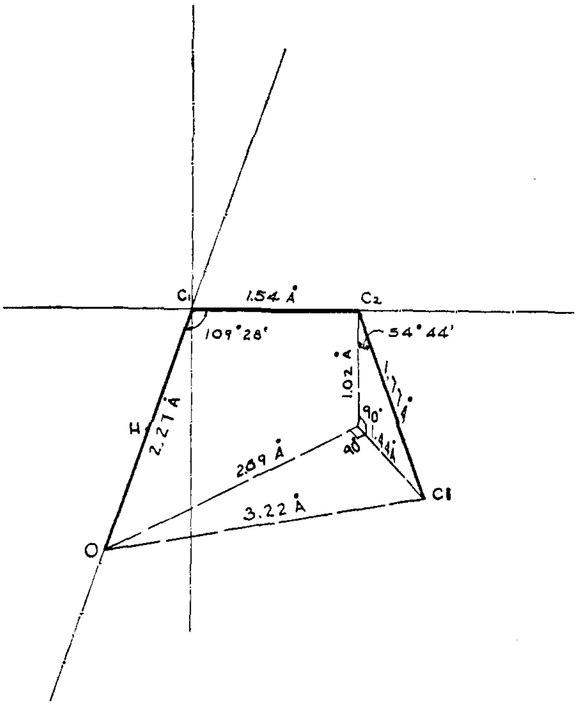

Fig. 4.—Diagram showing approximate transition-state distances involved in energy calculations for the *cis* configuration.

where E_c is the coulombic energy for a mole of such interactions, N is Avogadro's number, Z_1 is -1 for the hydroxyl group, μ is the bond dipole moment, ϵ is the charge on an electron, d is the carbon–chlorine bond distance, D is the effective dielectric constant of the medium, and r is the oxygen–chlorine distance in the model. Using equations (6) and (7), we obtain

$$\Delta E_c = -\frac{NZ_1(\mu/\epsilon\, d)\epsilon^2}{D}\left(\frac{1}{r_{cis}} - \frac{1}{r_{trans}}\right) \qquad (8)$$

assuming that the effective dielectric constant of the medium is identical for both cases. As we are interested in maximum limits for ΔE_c we have used a value for μ of 1.86 *D*. This value (the dipole moment of methyl chloride)[28] represents the highest possible value for the carbon–chlorine bond moment. Equation (8) then reduces to

$$\Delta E_c = 7.2/D \text{ kcal./mole} \qquad (9)$$

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[23] Ref. 20, p. 459.

[24] Normal covalent bond distances were taken from Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., Second Edition, 1940, pp. 167, 168.

[25] It should be noted that these distances for both *cis* and *trans* are greater than the sum of the van der Waals radii of the atoms concerned,[26] and that therefore there is no steric repulsion involved in this treatment. This assumption is based upon a model of the transition state in which no solvent molecules are involved. As pointed out by a Referee, in the reactions considered, both the hydroxyl group and the chlorine atom are solvated and the effective volumes are greater than those used above. A theoretical consequence of this solvated model is that compressions of solvent molecules can be avoided only by reduction of solvation in the *cis* reaction. Thus the energy of solvation will be decreased in the *cis* case over the *trans* case by a correction which we are unable to calculate. This comment is one of considerable significance, but the data of Dostrovsky, Hughes and Ingold[22] in substitution reactions show that experimental activation energies are in agreement with calculations of effects of steric hindrance upon activation energies when no hindrance due to solvent is considered. The quoted paper lends support to the assumption that differences in solvation energies will be of only minor significance in the case considered.

[26] Ref. 24, p. 189.

[27] See Amis, "Kinetics of Chemical Change in Solution," The Macmillan Co., New York, N. Y., 1949, p. 93, for a discussion of such calculations.

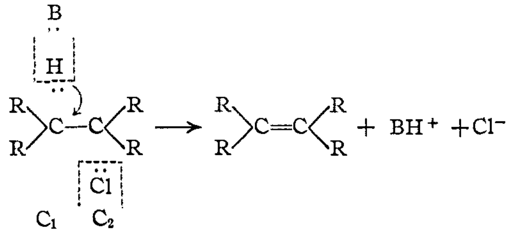
[28] Sänger and Steiger, *Helv. Phys. Acta*, **2**, 411 (1929); Sänger, *ibid.*, **3**, 161 (1930); Fuchs, *Z. Physik*, **63**, 824 (1930).

Values for ΔE_c ranging from 0.2 to 3.6 kcal./mole are obtained depending on the value for D used. If the value of 33 for the dielectric constant of 76% ethanol[29] is taken as the effective dielectric constant, the lower value for ΔE_c is obtained, whereas even with a value of 2 for D[30] a maximum value of 3.6 kcal./mole is obtained.

Use of Pauling's value for the carbon–chlorine bond moment[32] of 1.5 for μ rather than 1.86, reduces the limits of ΔE_c to 0.2 to 3.0 kcal./mole.

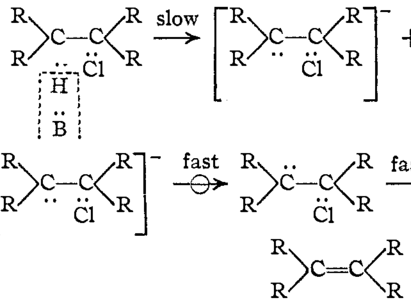
Thus, it seems apparent that only a small fraction of this large differential in rate and activation energy can be attributed to the greater repulsive forces in the *cis* system over the *trans*.

The superiority of the *trans* process has also been attributed[1b] to a difference in mechanism between it and the *cis* process. It was assumed that the *trans* process involved a one-stage *concerted* mechanism as


(10)

The base B attacks the hydrogen on carbon atom C_1, displacing the electron pair of the carbon–hydrogen bond which may simultaneously attack C_2 by a direct inversion process, forming the C_1–C_2 double bond and displacing chloride ion. This was considered as a smooth concerted process, the entire process occurring essentially together so that removal of the proton by base is facilitated by the formation of the double bond with loss of halide ion. This picture of *trans* elimination is analogous to that of the second-order nucleophilic displacement reaction with the entire process going smoothly through the transition state.[33]

It was assumed that for the concerted process, carbon C_2 must be in position to undergo inversion in the displacement of chloride ion by the electrons of the C_1–H bond undergoing rupture, requiring that the hydrogen and halide atoms be in *trans* position to each other. When free rotation is constrained around the C_1–C_2 bond so that the hydrogen and halide atoms are *cis* to each other, the above concerted process was not deemed possible, as inversion of C_2 is then not possible. It was suggested that under these circumstances the reaction then takes a course different from the one-stage process and represented by equations (11a) and (11b).

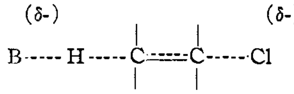

(11a)

(11b)

The first stage of this mechanism involves the slow, rate-determining removal of a proton by base, yielding a carbanion intermediate. This carbanion in a later fast step, decomposes to olefin and chloride ion, perhaps preceded by an inversion of the carbanion.[35] We shall call this the *two-stage* process.

The two-stage carbanion mechanism differs energy-wise and entropy-wise from the one-stage process by over-all reaction (11b). Usually this reaction is exothermic. For systems where neither the olefin nor the carbanion would be stabilized by resonance, the approximate heat of reaction (11b) may be calculated by the method of Remick[37] as −28 kcal./mole.[38] We may now apply the method of Polanyi and co-workers,[39] who have indicated, both experimentally and theoretically, that, in a series of analogous reactions, there is an inverse relationship between heat of reaction and activation energy. They calculated that a decrease in activation energy should result corresponding to approximately one-fourth to one-half of the increase in reaction heat.

Thus we may predict that the activation energy required to produce the transition state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[29] Akerlöf, THIS JOURNAL, **54**, 4125 (1932).

[30] This follows in part the argument of Kirkwood and Westheimer,[31] and assumes that the effective dielectric constant is that of the aliphatic skeleton which is arbitrarily taken as 2. We have been interested in limiting values for ΔE_c; more exact calculations could be made by setting up D as a function of r for each case and substituting this in an appropriate modification of equation (7). We do not plan to follow this through.

[31] Kirkwood and Westheimer, *J. Chem. Phys.*, **6**, 506 (1938).

[32] Ref. 24, p. 68.

[33] This mechanism has recently been restated by Ingold and co-workers,[34] and is similar to that usually accepted for E2 elimination,[8] with the additional restriction due to steric requirement.

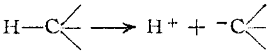
[34] Dhar, Hughes, Ingold, Mandour, Maw and Woolf, *J. Chem. Soc.*, 2093 (1948).

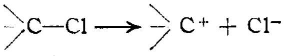
(35) The suggestion of inversion of the carbanion is made with the idea that this will enable displacement to occur more readily on C_2, and with the idea that carbanions are generally unable to maintain configuration,[36] but this step is not demonstrated in a kinetic study of this type.

(36) Ref. 19, p. 68.

(37) Remick, "Electronic Interpretations of Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1943, p. 219.

(38) This method divides the one-stage process formally into four hypothetical components as:

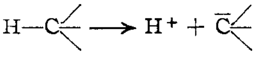

(12a)


(12b)

$$H^+ + OH^- \longrightarrow H_2O \qquad (12c)$$

$$>C^+—C^-< \longrightarrow >C{=}C< \qquad (12d)$$

and the rate-determining step of the two-stage process into

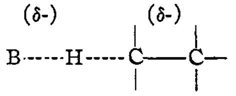

(13a)

$$H^+ + OH^- \longrightarrow H_2O \qquad (13b)$$

As (13a) and (13b) are identical with (12a) and (12c), the difference in heats of the two reactions can be estimated by the sum of the heats of hypothetical reactions (12b) and (12d). These have been estimated by Remick[37] as +240 and −268 kcal./mole, respectively, and the net advantage in reaction heat for the one-stage process is thus 28 kcal./mole.

(39) Ogg and Polanyi, *Trans. Faraday Soc.*, **31**, 1375 (1935); Evans and Polanyi, *ibid.*, **34**, 11 (1938); Polanyi, *Endeavour*, **8**, 3 (1949).

should be 7 to 14 kcal./mole lower than that required to produce the transition state



$$\overset{(\delta-)}{B}\cdots\cdots H\cdots\cdots \overset{|}{\underset{|}{C}}\overset{(\delta-)}{—}\overset{|}{\underset{|}{C}}— \qquad \text{II}$$

assuming, as mentioned above, no resonance stabilization of carbanion or olefin, and assuming further, that the solvation energies of both transition-state complexes would be approximately equal. The latter assumption seems valid since whatever apparent advantage transition state II might have in small charge dispersal[8] should be counteracted by difficulty of solvation due to steric hindrance at the carbanion carbon atom.[40]

The benzene hexachloride isomers are in accord with the above assumption that resonance effects are minimal, and the observation that the energy of activation for the β-isomer (*cis* elimination) is 9.6 to 12.5 kcal./mole higher than those for the other isomers (*trans* elimination) is in excellent agreement with the calculated estimates of 7–14 kcal./mole. Thus the major contribution to the superiority of the *trans* system over the *cis* system in elimination seems to be the existence of a concerted process for the *trans* system, with consequent lowering of activation energy, at least in cases where resonance effects are small.[41]

Dehydrochlorination of δ-Benzene Hexachloride.—To an ice-cold solution of 0.985 g. (0.0034 mole) of δ-benzene hexachloride in 15 ml. of 95% ethyl alcohol was added 6.98 ml. of 0.485 *N* NaOH solution over a period of 40 minutes. The reaction mixture was allowed to stand for 90 minutes in an ice-bath, after which time, the solution had become neutral. Seventy-five ml. of water was added, and the solution was placed in a refrigerator. After standing 24 hours, the reaction mixture was filtered and 480 mg. (0.0023 mole) of crystalline product was obtained, m.p. 55–62°. After recrystallizations from aqueous ethanol and drying over phosphorus pentoxide the material melted at 68–68.5° (cor.).

Anal.[42] Calcd. for $C_6H_5Cl_5$: C, 28.33; H, 1.98; Cl, 69.69. Found: C, 28.56; H, 2.14; Cl, 69.61.

This compound thus has an analysis corresponding to that of a pentachlorocyclohexene. We hope to continue work on its structure.

Materials Used.—The samples of the α-, β-, γ- and δ-isomers were those described previously.[1b] The ε-isomer[43] was kindly furnished by Mr. W. W. Allen of the Dow Chemical Company, and was recrystallized to constant m.p. 219–220° (cor.), and dried *in vacuo* before use.

Summary

A study has been made of the rates of dehydrochlorination with sodium hydroxide in 76.1% ethanol of four of the isomers of benzene hexachloride. The β-isomer, in which all vicinal pairs of hydrogen and chlorine atoms are *cis*, reacts at a rate 7000 to 24000 times slower, and with activation energies 9.6 to 12.5 kcal./mole greater, than the α-, γ- and ε-isomers, where *trans* elimination is possible.

The possibility that repulsive forces are the major contributors to this superiority of *trans* elimination over *cis* is considered and shown to be unlikely. The data seem best explained on the basis of two different mechanisms for elimination. One, *trans* elimination, involves a one-stage concerted process, in which the proton is removed, the double bond is formed, and halide ion is evolved in one step. The second, apparently observed in *cis* elimination, involves a multiple-stage process, in which only the proton is removed in the rate-determining step, yielding a carbanion intermediate. Approximate calculations of activation energy differences for these two processes are in agreement with observed differences.

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[40] von Egidy, M.A. thesis, University of Colorado, 1949.

[41] A case where this is not true will be discussed in a later paper.

[42] Analysis by H. S. Clark, Urbana, Illinois.

[43] Kauer, DuVall and Alquist, *Ind. Eng. Chem.*, **39**, 1335 (1947).

BOULDER, COLORADO RECEIVED MAY 15, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PORTLAND]

Dehydrobromination of α,β-Dibromohydrocinnamic Acid in Liquid Ammonia[1]

BY R. V. PAULSON[1] AND WARREN S. MACGREGOR

The dehydrobromination of sodium α,β-dibromohydrocinnamate with aqueous or alcoholic alkalies at room temperature or at the boiling point has been shown to yield mixtures of *cis*- and *trans*-α-bromocinnamic acids when two equivalent amounts of alkali were used and phenylpropiolic acid when three or more equivalents were used.[2] The two β-bromocinnamic acids generally have been obtained, not by dehydrobromination, but from the addition of hydrogen bromide to phenylpropiolic acid.[3] When the addition was conducted in aqueous, acetic acid, or alcoholic solution the principal products were the two β-bromocinnamic acids while in carbon disulfide or benzene solutions the main product was α-bromo-*trans*-cinnamic acid.[4] This change in the mode of addition was represented by Michael[5] as a solvent effect that was particularly evident because all four of the olefinic acids had approximately the same heats of formation.

The course of the dehydrobromination of α,β-dibromohydrocinnamic acid might be expected to show a similar response to solvent change if the activation energies of the reaction paths leading to the α- or β-bromocinnamic acids were not too different. Such an alteration was encountered when liquid ammonia rather than water or alcohol was used as the solvent for the dehydrobromination with sodium ethoxide. The reaction of ammonium α,β-dibromohydrocinnamate in liquid ammonia with sodium ethoxide was rapid and occurred in well-defined steps. The first equivalent of sodium ethoxide was consumed in reaction with the ammonium

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[1] From the M.S. Thesis of R. V. Paulson, August, 1949.

[2] Sudborough and Thompson, *J. Chem. Soc.*, **83**, 666 (1903).

[3] Michael and Brown, *Ber.*, **19**, 1397 (1886).

[4] Sudborough and Thompson, *J. Chem. Soc.*, **83**, 1153 (1903).

[5] Michael, *J. Org. Chem.*, **4**, 128 (1939).